State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

APPENDICES

FOR THE

Report for Air Monitoring Around a Structural Application of Sulfuryl Fluoride in Loomis, CA Summer - 2004

Operations Planning and Assessment Section
Quality Management Branch
Monitoring and Laboratory Division

Project No. P-03-002

Date:
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MONITORING PROTOCOL

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

Protocol for Air Monitoring
Around a Structural Fumigation Application
of Sulfuryl Fluoride and Chloropicrin
Spring 2004

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This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Spring 2004

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR) (October 18, 2002 Memorandum, Helliker to Lloyd), the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticides sulfuryl fluoride and chloropicrin around a structural fumigation application, tentatively scheduled to be conducted in Spring 2004. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions...of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The product label for sulfuryl fluoride (Vikane®) requires that Chloropicrin be used as a warning agent during the fumigation. Monitoring will be conducted for both sulfuryl fluoride and chloropicrin around a single structural application. The study will be conducted around a fumigation for powderpost beetles, which requires an elevated level of fumigant relative to structural fumigation for other pests (e.g., termites).

The sampling and analysis will follow the procedures outlined in this protocol as well as the procedures described in Attachment I, "Standard Operating Procedure for the Determination of Sulfuryl Fluoride Measured as Fluoride by Ion Chromatography" (January 14, 2004 Version) and Attachment II, "Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector" (10/29/02 Version).

II. Sampling

Sulfuryl fluoride samples will be collected on charcoal (coconut shell) sampling cartridges at a sample collection flow rate of 50 standard cubic centimeters per minute (sccpm). Two cartridges in series will be used for sample collection during the "mechanical aeration" sampling period at all sampling stations. Only one sampling cartridge will be used for all other sampling periods.

Chloropicrin samples will be collected on XAD-4 resin sampling cartridges. For chloropicrin, the tubes are 8 mm x 140 mm, XAD-4, with 400 mg in the primary section, and 200 mg in the secondary section (SKC special order). Sample collection is at a flow rate of 100 standard cubic centimeters per minute (sccpm).

Subsequent to sampling, the tubes are capped, labeled, placed in a culture tube, and stored and transported in an insulated container with dry ice. The samples are

transported (driven) to the ARB laboratory in Sacramento.

Caution should be used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo-degradation of chloropicrin.

Each sample train consists of an adsorbent tube, Teflon fittings and tubing, rain/sun shield, needle valve, PVC manifold train support, and a 12 volt DC vacuum pump (see Figure 1). Each tube is prepared in the field by breaking off each sealed glass end and then immediately inserting the tube into the fitting. The tubes are oriented in the sample train with a small arrow printed on the side of each tube indicating the direction of flow. Needle valves will be used to control the flow rate for sampling. The flow rates will be set using a calibrated digital mass flow meter (MFM) before the start of each sampling period. The MFMs used for the chloropicrin and sulfuryl fluoride samplers have a range of 0-200 sccpm. The MFMs have been calibrated to standard conditions (1 atm and 25 °C). The flow rate is also checked and recorded, using the MFMs, at the end of each sampling period. Any change in flow rates will be recorded in the field logbook (see Attachment V). The pesticide sampling procedures for adsorbent tubes are included as Attachment IV.

The fumigation process for powderpost beetles is expected to consist of a 36 to 72 hour exposure, a 1 to 2 hour mechanical vent period, followed by an 8 to 48 hour aeration period. The intention of this study is to target a fumigation using a shorter exposure period (i.e., 36 to 48 hours rather than 72 hours) as higher Vikane® application rates are required for the shorter exposure periods. The "mechanical vent" is conducted at the end of the exposure period, just prior to removal of the tarps. The purpose of the "mechanical venting" is to remove the gas between the tarp and the structure to minimize occupational exposure during removal of the tarps. For the purpose of this study, "mechanical venting" will be defined as ending and aeration as starting when the tarps are completely removed.

The aeration period required by the product label is a minimum of 8 hours. However, fumigation companies may choose to aerate the structure for a longer period of time. As per the Monitoring Recommendations, "DPR does not specify a preference of aeration method for the monitoring study."

This study will target a fumigation using a 24-hour aeration period (i.e., reentry for sampling personnel should be cleared after 24 hours of aeration). The structure cannot be reentered until it is "cleared" as having Vikane® concentrations of less than 5 ppmv. The fumigator uses a Miran or Interscan gas analyzer to measure the Vikane® concentration to clear the structure for reentry.

The sampling schedule shown in Table 1 is intended as a guide. Exact sampling periods will be defined after the specific monitoring location is selected and the fumigation schedule determined.

Table 1
Fumigation Sampling Schedule

Sample period begins	**Sample duration time**
Background (pre-fumigation)	24 hours
Fumigation start	Start of fumigation until 1 hour before sunset
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until mechanical aeration begins); do not have to sample if this period will be less than 3 hours
Start of mechanical aeration	Until the tarp is completely removed (about 1.5 hours)
Beginning of Aeration	Until 1 hour before sunset
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Until end of Aeration (when cleared): do not have to sample if this period will be less than 3 hours
End of Aeration (if before noon)	*Until 1 hour before sunset*
End of Aeration (if after noon)	*Until 1 hour after sunrise*
As appropriate based on the time of aeration end	
1 hour before sunset or,	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)

In addition, after completion of aeration (i.e., when the structure is cleared), two 24-hour samples will be taken at each of two different locations inside the fumigated structure (total of four samples).

The application monitoring study will be conducted at the location and under the conditions described in Table 2.

Table 2
Application Information

Location:	To Be Determined (TBD) (Sacramento area)
Type of Structure:	TBD (most likely a house)
Size of Structure:	Target size of 26,000 cubic feet or greater (smaller structures will be considered if all other site parameters are met)
Product Applied:	Vikane®, chloropicrin
Type of Application:	Structural
Pest controlled:	Powderpost Beetle
Application Rate:	TBD (at "10x ounce hours" for sulfuryl fluoride) (target 1 ounces chloropicrin per 10,000 cubic feet)
Applicator:	TBD
Duration of Fumigation:	TBD (36 to 48 hours expected)
Duration of Vent	TBD (1 to 2 hours expected)
Duration of Aeration:	TBD (24 hours expected)

The structure selected for monitoring must have enough clearance surrounding it to allow for sampler placement (unobstructed) at a distance of 5, 10 and 30 to 50 feet from the edge of the structure. Per the DPR's request, 12 samplers will be placed surrounding the structure in 3 rings. The first ring consists of four samplers located at the middle of and 5 feet from each side of the structure. The second ring consists of four samplers 10 feet out from each corner of the structure. The third ring contains four samplers which would be placed 30 to 50 feet from each side or corner of the structure. If possible, all the third ring samplers will be positioned at the same distance from the structure. A thirteenth sampler will be collocated with one sampler in the first ring and at the site expected to be downwind during mechanical venting and aeration. The collocated sample will be collected at this site during each sampling interval. Sample inlets should be 1.5 to 2.0 meters above the ground.

Two additional samplers will be used during the "mechanical aeration" stage and will be placed downwind of the structure approximately 40 feet beyond the 3rd ring. Two more samplers will be placed inside the structure for collection of post-aeration samples. Background samples will be collected at the four corner (2nd ring) locations for 24 hours prior to the fumigation.

In regard to field data, the monitoring report will include:

1) An accurate record of the positions of the monitoring equipment with respect to the structure, including the exact direction and distance of the samplers from the edge of the structure and a record of three dimensions of the structure (length, width, height);
2) An accurate record of pesticide application, including application time, method, dosage (rate), fumigation duration, aeration method and duration;
3) An accurate drawing of the monitoring site showing the precise location of the

samplers, meteorological equipment, trees, other buildings and other obstacles with respect to true North,

4) meteorological data collected at 5-minute intervals including wind speed (mph) and direction, humidity, and air temperature and comments regarding degree of cloud cover, (as well as the exact location of the met station) and
5) the elevation of each sampling station with respect to the ground level (grade) of the structure.

III. Analysis

The sampling and analysis method and updated validation results for sulfuryl fluoride are included as Attachments I and VI, respectively.

The exposed charcoal sorbent tubes are frozen until desorbed with 10 milliliters (ml) of 40 millimolar (mM) sodium hydroxide (NaOH). An aliquot of the charcoal extract is evaporated to dryness and reconstituted with deionized water. Fluoride ion in the extract is separated by an anion exchange chromatographic method which employs an isocratic mobile phase and chemical suppression of background conductivity. The method detection limit (MDL) and estimated quantitation limit (EQL), expressed as fluoride, are 0.0859 ug/ml and 0.429 ug/ml, respectively. Based on a 10 ml extraction volume and molecular weight conversion factor of 102/38, the MDL and EQL expressed as sulfuryl fluoride are 2.31 ug/sample and 11.5ug/sample, respectively. For a 24-hour sample at 50 sccpm (0.072 cubic meters), the MDL and EQL, expressed as sulfuryl fluoride, would be 32.1 ug/m^3 and 160 ug/m^3, respectively. The DPR target EQL was 30 ug/m^3.

The sampling and analysis method (including a summary of validation results) for the chloropicrin are included as Attachment II. The chloropicrin method will consist of sampling with XAD-4 resin cartridges along with GC analysis with mass selective detector. The method detection limit (MDL) and estimated quantitation limit (EQL) for chloropicrin are 3.96 ng/sample and 19.8 ng/sample, respectively. For a 24-hour sample at 100 sccpm, the MDL and EQL would be 27.5 ng/m^3 and 138 ng/m^3, respectively. The DPR target EQL was 100 ng/m^3.

The analyses will be performed by the ARB laboratory in Sacramento.

IV. Field Quality Assurance

Field Quality Control for the structural monitoring will include the following:

1) Normally four field spikes are obtained during a study by sampling ambient air at the structural fumigation monitoring site for 24 hours. However, due to an issue with the validity of field spikes generated with the traditional spiking method (syringe injection of standard onto the

cartridge) the sulfuryl fluoride field spikes will be generated using a dynamic spiking procedure. The sulfury fluoride field spikes will be collected at the ARB 14th and S facility at the same time that the fumigation test is taking place in Sacramento. Four dynamic spikes will be collected (2 daytime and 2 overnight). For chloropicrin, four field spikes will be collected, two at the site during the background sampling and two along with the sulfuryl fluoride dynamic spikes (but will be run for 24 hours).

2) Four trip spikes each will be prepared for sulfuryl fluoride and chloropicrin. The chloropicrin trip spikes will be prepared at the same level as the field spikes. The trip spikes will be labeled, recorded on the field log-sheet, and transported along with the chloropicrin field spikes and application samples.

3) Four lab spikes each will be prepared for sulfuryl fluoride and chloropicrin at the same level as the trip spikes (and field spikes for chloropicrin). The lab spikes will remain in the laboratory freezer and will be extracted and analyzed along with the field and trip spikes.

4) Collocated (replicate) samples will be taken for all sampling periods (except the background period) at one sampling location (downwind).

5) A trip blank will be obtained, labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

The traditional method of spiking the charcoal cartridges with sulfuryl fluoride is to use a gas tight syringe to inject a known volume of a sulfuryl fluoride gas standard onto the glass wool at the front of the cartridge. The standard gas is injected while air is pulled through the tube for a short period of time (e.g., 10 seconds). The available data indicate that field spikes run using this traditional spiking method do not provide results that reflect actual sampling conditions. Samples spiked in the above fashion followed by sampling of ambient air show high recoveries (>90%) regardless of the sampling flow rate used (e.g., 50 ccpm, 1 lpm or 3 lpm). Furthermore, no migration of the sulfuryl fluoride from the primary charcoal bed to the secondary bed (breakthrough) was observed, even at a sampling rate of 3 lpm for a 24-hour period. This quantitative retention on the primary bed was confirmed with the field spikes run during a previous structural fumigation study ("Report for Air Monitoring Around a Structural Application of Sulfuryl Fluoride, Fall- 2002", June 18, 2003). However, <u>all</u> actual samples collected during that study with detectable levels of sulfuryl fluoride showed breakthrough from the primary bed to the secondary bed at a sampling rate of 1 lpm, regardless of sampling duration (shortest time was about 1.5 hours). In addition, four samples were collected using 2 charcoal cartridges in series. The results of those samples indicates that the sulfuryl fluoride was not effectively retained even by two cartridges in series (4 charcoal beds).

Later method development work showed that use of a dynamic spiking procedure was necessary in order to accurately reflect sampling conditions for sulfuryl fluoride in ambient air. The dynamic spiking system mixes a known volume of standard gas with ambient air prior to passing into the sampling cartridge. Thus a known concentration of sulfuryl fluoride in ambient air is generated that can be sampled through a charcoal cartridge for the sampling duration and at the sampling flow rate used for actual sampling. Using this system it was shown that breakthrough occurred at sampling flow rates over 50 ccpm.

The dynamic spike procedure is not suitable for use on-site during the test. Therefore, for this test the "traditional" spiking method will be used to make the sulfuryl fluoride lab and trip spikes and the field spikes will be generated using the dynamic spik procedure at the ARB 14th and S facility.

V. Personnel

ARB sampling personnel will consist of Air Quality Surveillance Branch staff.

VI. Safety Recommendations

It is the policy of the ARB that health and safety is an integral part of every operation. The safety of field staff will be the first consideration in all field operations and ARB staff and management will comply with all laws and regulations pertaining to safety of employees while in the field. No ARB employee will be required to work at a job he/she knows is not safe or healthy.

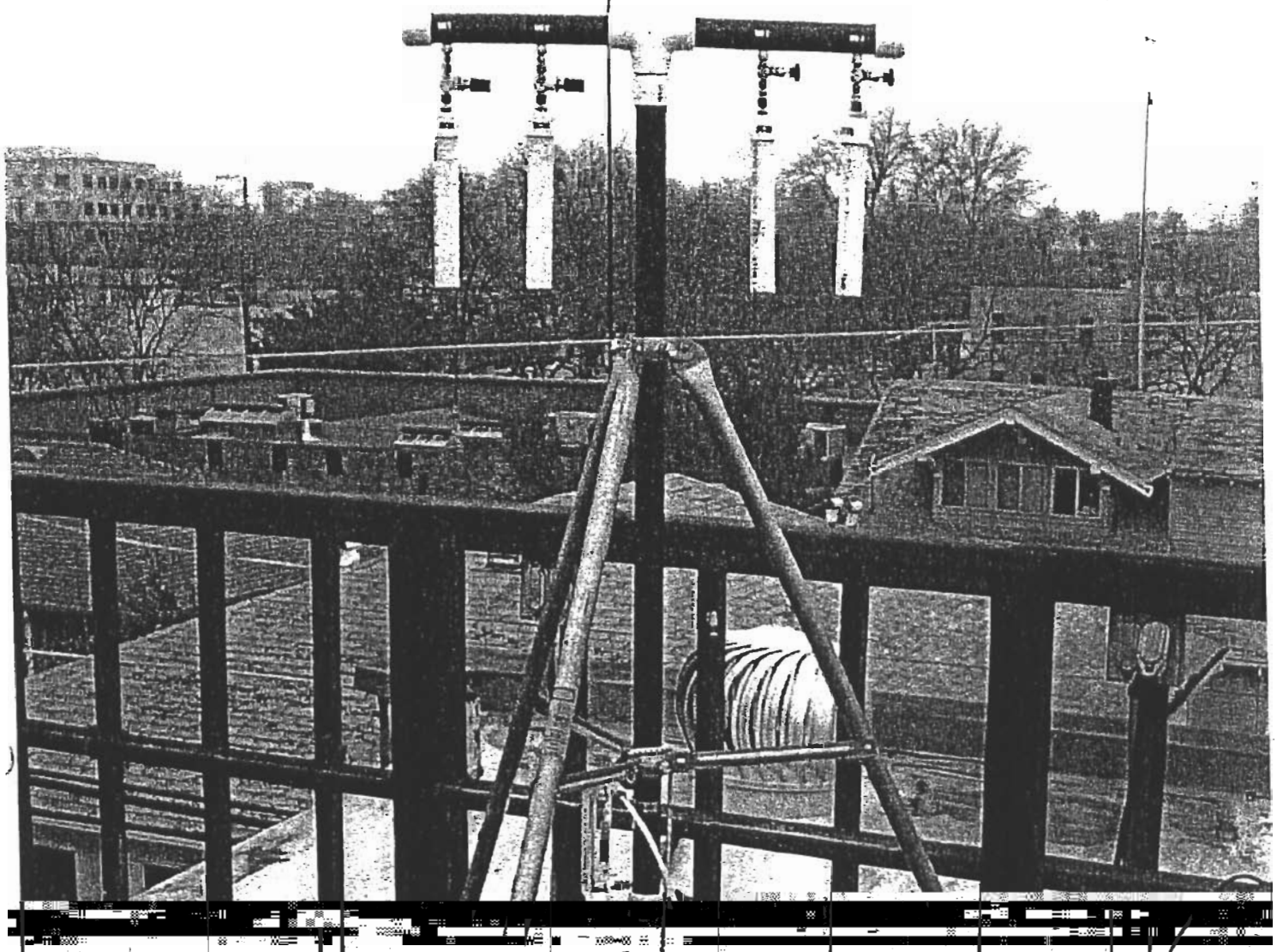
The following paragraphs describe DPR's safety recommendations regarding structural fumigation applications using Vikane. Refer to Attachment V for general information on and toxicology of Vikane gas fumigant.

> "Most of the following safety precautions pertain to applicators. In this recommendation, the sampling schedule is arranged to prevent sampling personnel from being near the structure during application. Therefore, most of these precautions are for reference only.
>
> Product labels for the fumigants carry a danger warning. Inhalation of the vapors may be fatal or cause acute illness or delayed lung or nervous system injury if exposed to high concentrations. Do not get in eyes, on skin, or on clothing. Chloropicrin is also a strong lachrymator causing painful irritation to the nose and throat and causing tearing of the eyes. The labels recommend application personnel wear loose-fitting or well-ventilated long-sleeve shirt and long pants, and socks and shoes; chloropicrin also requires a full-face shield or safety glasses with brow and temple shields."

The highest ambient concentrations are expected during the 'mechanical vent' period. The DPR estimates, from tests conducted by the registrants, that the concentration of sulfuryl fluoride may be from 25,000 ug/m^3 (6 ppmv) to 70,000 ug/m^3 (17 ppmv) in the area surrounding the vent tube during the initial part of the mechanical vent period. However, the registrant tests showed that the ambient sulfuryl fluoride concentration decreased to below the monitoring detection limit of 0.006 ppmv (25 ug/m^3) at the start of aeration (e.g., after the tarp is removed). In order to insure the safety of sampling personnel, the "mechanical vent" period samples will be started just prior to turning on the "mechanical vent" fan. The "mechanical vent" sampling period for this study will end at the start of the aeration period (i.e., after tarp removal). Thus, sampling personnel will not be present during the mechanical vent period and so will not be exposed to the potentially higher levels present during that time. Structures may be reoccupied when concentrations of sulfuryl fluoride are 5 ppmv or less (as per the product label requirements).

MANIFOLD SAMPLER

01/29/02



Attachment I

Standard Operating Procedure
for the Determination of Sulfuryl Fluoride
Measured as Fluoride by Ion Chromatography

California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

Standard Operating Procedure for the Determination of Sulfuryl Fluoride Measured as Fluoride by Ion Chromatography

January 14, 2004

Approved by:

Russell Grace, Manager
Special Analysis Section

This SOP has been reviewed by staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names of commercial products constitute endorsement or recommendation for use.

1. SCOPE

This document describes an ion chromatography (IC) procedure for the determination of sulfuryl fluoride, measured as fluoride (F-), from air samples collected on charcoal sorbent tubes. The Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) to do application and structural monitoring of sulfuryl fluoride at an estimated quantitation limit (EQL) of 30 micrograms per cubic meter ($\mu g/m^3$).

2. SUMMARY OF METHOD

Air samples are collected on charcoal sorbent tubes at a flow rate of fifty (50) milliliters per minute (ml/min) over various time periods. The exposed charcoal sorbent tubes are stored in a freezer until desorbed with ten milliliters (ml) of 40 millimolar (mM) sodium hydroxide (NaOH). An aliquot of the charcoal extract is evaporated to dryness and reconstituted to volume with deionized water. Fluoride ion in the extract is separated by an anion exchange chromatographic method which employs an isocratic mobile phase and chemical suppression of background conductivity.

3. INTERFERENCES/LIMITATIONS

Method interference may be caused by contaminants in sorbent tubes, reagents, glassware or other processing apparatus that lead to discrete artifacts or elevated baselines. A method blank must accompany all quantitation runs to detect method interference.

Matrix interference may be caused by ambient contaminants that extract from the sample. The extent of matrix interference may vary from source to source.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION

Ion Chromatograph: Dionex DX-500
Pump, isocratic at 1.0 ml/min: Dionex GP 50
Chromatography Enclosure: Dionex LC20
Detector: Dionex CD20 Conductivity Detector
Printer: HP Laserjet 4100
PC: Dell OptiPlex G1
Column: Dionex AS14 Ion Pac 4x250 mm
Guard column: Dionex AG14 Ion Pac 4x50 mm
Supressor: Dionex ASRS-Ultra 4 mm

Auto Sampler:
Vial type – 0.5 ml

Setup – injection type = loop, 25 µl
Injection mode = proportional
Bleed = off
inj/vial = 1

B. AUXILIARY APPARATUS:

1. Desorption vials, VWR 20 ml with teflon screw caps
2. Sampler vials, Dionex 0.5 ml
3. Syringe, Gastight
4. Syringe filter units, Whatman 1.0µm PTFE
5. Disposable syringes, 3 ml
6. Hot plate, Corning PC-420
7. Sonicator, Branson 1200

C. REAGENTS

1. 10 N NaOH, reagent grade
2. IC mobile phase and sample desorbant, 40 mM NaOH, 8 ml 10 N NaOH dilute to 2 liters with deionized water
3. Sorbent tubes, SKC coconut charcoal (SKC 226-16)
4. Fluoride standard, Dionex 1000 +/- 14 mg/L in deionized water
5. Sulfuryl fluoride gas standard, 32.9 ppm +/- 2%, Scott-Marrin

5. ANALYSIS OF SAMPLES

5.1 The field samples are collected on charcoal sorbent tubes which are stored in a freezer after exposure and before desorption.

5.2 Remove the glass wool plug from the primary end of the charcoal tube with forceps. Pour the primary resin bed into a 20 ml desorbing vial and add 10 ml of 40 mM NaOH to the vial. Cap the vial tightly. Retain the secondary section of the charcoal tube resin bed for later analyses.

5.3 Place the desorbing vial into the sonicator for 1 hour. Filter the NaOH extract through a 1.0 µm syringe filter. Put 5 ml of the extract into a clean 20 ml desorption vial. Place the uncapped extract vial on a hotplate and evaporate to dryness.

5.4 Remove the vial from the hot plate and allow to cool. Reconstitute the vial with 5 ml of deionized water and mix the vial contents thoroughly. The contents of the vial are now ready for IC analysis.

5.5 Establish HPLC operating parameters by using Chromeleon software. From the Browser screen select the equilibrate icon and monitor the detector signal. When baseline is stable the IC is ready for analysis.

5.6 Create an analysis worklist which contains the following elements: a set of six calibration standards, a reagent blank, a charcoal resin extraction blank, a lower calibration range charcoal gas spike and a high calibration range charcoal gas spike. A calibration check sample should be analyzed after each group of ten field samples and at the end of the analysis batch. When creating a worklist use file name SO2F2a for the worklist program and fluoride for the worklist method file.

5.7 The autosampler is setup by pouring 0.5 ml of sample into 0.5 ml sample vials and loading the vials into sample carriers in the same order as the sample schedule. Autosampler parameters are not set automatically when the method is loaded, so they must be checked before a sample run is started.

5.8 A sample batch can be submitted for analysis from the browser software by clicking on the batch start icon.

5.9 Method calibration is automatically updated by designating calibrators on the worklist. Atmospheric concentration is calculated according to:

Conc., $\mu g/m^3$ = (Amount, μg/ml X 10.0 ml) /Air Volume Sampled, m^3

6. QUALITY ASSURANCE

A. INSTRUMENT REPRODUCIBILITY

Five injections of standards at three concentrations are made in order to establish the reproducibility of the instrument. The concentrations used should be at the high, middle and low areas of the calibration range. Method development studies for the current method version showed: low level - cv (coefficient of variation) = 12.1%, medium level - cv = 2.1%, high level - cv = 2.5%.

B. CALIBRATION

A calibration curve is determined by linear regression analysis of six calibration standards. The correlation coefficient for the linear regression must be 0.995 or greater.

C. CALIBRATION CHECK

A calibration check sample is run after every tenth field sample to verify system calibration. Calibration check samples must be within 10% of the assigned value. If the check sample is out of range then the affected samples must be reanalyzed.

D. MINIMUM DETECTION LIMIT

The minimum detection limit (MDL) is based on USEPA MDL calculation. Using the analysis of seven replicates of a low level matrix spike, the MDL and the estimated quantitation limit (EQL) for fluoride were calculated by:

$$MDL = 3.14*s$$

$$EQL = 5*MDL$$

where: s = the standard deviation of the concentration calculated for the seven replicate spikes. Given s = 0.027 ng/ml for the seven samples, the MDL and EQL for fluoride are calculated as follows.

$$MDL = 3.14\ (0.027\ \mu g\ /ml) = 0.086\ \mu g\ /ml\ fluoride$$

$$EQL = 5\ (0.086\ \mu g\ /ml) = 0.43\ \mu g\ /ml\ fluoride$$

Based on the 10.0 ml extraction volume and assuming a sample volume of 0.072 m^3 (50 ml/min for 24 hours) the MDL and EQL for ambient concentration of fluoride are:

$$MDL = (0.086\ \mu g\ /ml)\ (10ml)\ /\ 0.072\ m^3 = 11.9\ \mu g\ /\ m^3\ fluoride$$

$$EQL = 5\ (11.9\ \mu g\ /\ m^3) = 59.6\ \mu g\ /\ m^3\ fluoride$$

The equivalent MDL and EQL expressed as sulfuryl fluoride for a **24 hour** sample are:

$$MDL = (11.9\ \mu g\ /\ m^3\ )\ (102/38) = 31.9\ \mu g\ /\ m^3\ sulfuryl\ fluoride$$

$$EQL = (59.6\ \mu g\ /\ m^3\ )\ (102/38) = 160\ \mu g\ /\ m^3\ sulfuryl\ fluoride$$

Samples collected for less than 24 hours will have proportionally higher MDL and EQL values.

E. EXTRACTION EFFICIENCY

Extraction efficiency is established by extracting and analyzing spiked sorbent tubes that are not exposed to field sampling conditions. Three replicates at two levels are extracted with the average and standard deviation determined for the replicates. The average amount divided by the amount added and multiplied by 100 gives the percent recovery. Method development results for the current

version of the method are: 20.6 μg spike results have 83% average recovery, 55.1μg spike results have 90% average recovery.

F. COLLECTION EFFICIENCY

Collection efficiency is established by extracting and analyzing spiked sorbent tubes that have been exposed to field sampling conditions. Three replicates at two levels are extracted with the average and standard deviation determined for the replicates. The average amount divided by the amount added multiplied by 100 gives the percent recovery. For the current method a 123 μg spike has an average recovery of 89% and a 330 μg spike has an average recovery of 81%.

G. STORAGE STABILITY

A storage stability study is conducted over a six-week period. Tubes are spiked with sulfuryl fluoride gas at low and high calibration levels. The spiked tubes are stored in the freezer at -20°C and extracted/analyzed at spaced time intervals. Method development results for the current method version show that samples stored in the freezer are stable for at least six (6) weeks.

H. BREAKTHROUGH

For the current method version a " dynamic" spiking technique was used to evaluate breakthrough. A known amount of sulfuryl fluoride was spiked into a sample stream and collected on a charcoal tube. Total sample flow was 50 ml/min. The secondary charcoal bed was extracted and analyzed for fluoride. The average breakthrough for a 123 μg spike was less than EQL and for a 330 μg spike was 7.6 %.

7. SAFETY

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. Therefore, each chemical compound must be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level. Material safety data sheets (MSDS's) should be on file for all analytes and reagents.

Attachment II

Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector

California Environmental Protection Agency

Air Resources Board

Standard Operating Procedure for
Sampling and Analysis of Trichloronitromethane
(Chloropicrin) in Application and Ambient Air using Gas
Chromatography/Mass Selective Detector

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

Revision 1
10/29/02

Approved by:

Russell Grace, Manager
Special Analysis Section

DISCLAIMER: Mention of any trade name or commercial product in this Standard Operating Procedure does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

1. SCOPE

The current method is for the analysis of trichloronitromethane (TCNM) using a gas chromatograph/mass selective detector. The procedure is for the analysis of application and ambient air monitoring of TCNM using XAD-4 resin tubes. The Department of Pesticide Regulation (DPR) asked the Air Resources Board (ARB) to analyze for TCNM during agricultural/structural application with a requested quantitation limit of 1.0 $\mu g/m^3$ and ambient monitoring with a quantitation limit of 0.1 $\mu g/m^3$.

2. SUMMARY OF METHOD

Resin tubes, XAD-4, are placed on the sampler for 24 hours at a flowrate of 0.1 liters per minute (LPM or 100 mLPM). The samples are stored in an ice chest or refrigerator until extracted with 3.0 ml of dichloromethane (DCM). A gas chromatograph with a mass selective detector in the selected ion monitoring (SIM) mode is used for analysis.

3. INTERFERENCES/LIMITATIONS

Interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. A method blank, including both solvent and resin, must be analyzed with each batch of samples to detect any possible interferences.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:

Hewlett-Packard 6890 Series gas chromatograph
Hewlett-Packard 5973 Network mass selective detector
Hewlett-Packard 6890 Enhanced Parameters ALS

MS Transfer line: 280°C
Injector: 210°C, Splitless, Liner 4 mm straight liner with glass wool
Column: Restek Rtx-200, 60 meter, 320 µm i.d., 1.5 µm film thickness, or equivalent

GC Temperature Program: Oven initial 40°C, hold 4 min. Ramp to 220°C @ 12°C/min., hold 1 min., ramp to 240°C @ 20°C/min., hold 2.0 min.
Retention time: TCNM 11.93 min.

Splitter open @ 1.0 min.
Flows: Column: He, 1.6 ml/min, 9.1psi. (velocity: 32cm/sec)
Splitter: 50 ml/min.

Mass Spectrometer: Electron Ionization
Selective Ion Monitoring: trichloronitromethane: 117 (quant. ion 100%), 119 (qual. ion 98%); Tuning: PFTBA on masses 69, 219, 502

B. Auxiliary Apparatus

1. Precleaned vials, 8 ml capacity with teflon caps
2. Whatman filters, 0.45 µm
3. Disposable syringes, 3 ml
4. Sonicator
5. GC vials with septum caps

C. Reagents

1. Dichloromethane, Pesticide grade or better
2. Trichloronitromethane, Chem Service PS-4, 98.8%
3. XAD-4 resin sorbent tubes, 400/200mg, SKC, Fullerton, CA

5. ANALYSIS OF SAMPLES

1. A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses: 69, 219, 502. The criterion for the tune are the peak widths at ½ the peak height, 0.60 ± 0.05, and the criteria for relative abundance: 69:100%, 219:90-120%, and 502: 5-12%.

2. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample that may result in possible carry-over contamination.

3. A five-point calibration curve shall be analyzed with each batch of samples. For the ambient studies the calibration will be 5.0-50.0 ng/mL and for the application studies 50.0-500 ng/mL.

4. A calibration check sample (7.5 ng/ml for ambient, and 75 ng/ml for application) is run after the calibration, after every ten samples and at the end of the sample batch. The value of the calibration check must be within $\pm 3\sigma$ (the standard deviation) or ±10% of the expected value whichever is greater. If the calibration check is outside this limit, then those samples in the batch after the last calibration check that was within limits need to be reanalyzed.

5. With each batch of samples analyzed, a laboratory blank and a laboratory control spike will be run concurrently. A laboratory blank is XAD-4 extracted and analyzed the same way as the samples. A laboratory control spike is XAD-4 spiked with a known amount of standard. The laboratory control

sample is extracted and analyzed the same way as the samples. Laboratory control samples should have recoveries that are greater than or equal to 70% of the theoretical spiked value.

6. Score and snap the sample resin tube, transfer the front bed of the resin tube into an 8-ml vial. (Save the back-up bed for future analysis if necessary.) Rinse the tube with 3.0 ml of DCM into the extraction vial. Cap and place the vial in the sonicator for one hour.

7. Filter the samples using 0.45 µm filter attached to a 3-ml syringe directly into a GC vial and cap securely.

8. The atmospheric concentration is calculated according to:

$$\text{Conc } (ng/m^3) = \text{Extract Conc } (ng/ml) \times 3 \text{ ml} / \text{Air Volume Sampled } (m^3)$$

6. QUALITY ASSURANCE

A. Instrument Reproducibility

The reproducibility of the instrument and analytical method was established by analyzing five (5) 1.0 µl injections of trichloronitromethane standard at three concentrations (low, mid, and high). The low, mid and high concentrations were 5, 20 and 50 ng/ml, respectively.

B. Calibration

A five-point calibration curve is made ranging from 5.0 ng/ml to 50.0 ng/ml for ambient monitoring and 50 ng/ml to 500 ng/ml for application monitoring.

C. Calibration Check

A calibration check sample is run after the calibration, after every ten samples and at the end of the sample batch to verify the system is in calibration. The value of the check must be within $\pm 3\sigma$ (the standard deviation) or $\pm 10\%$ of the expected value whichever is greater. If the calibration check is outside the limit, then those samples in the batch after the last calibration check that was within the limit need to be reanalyzed.

D. Minimum Detection Limit

The detection limit is based on US EPA MDL calculation. Using the analysis of seven (7) replicates of a low-level matrix spike, the method detection limit (MDL) and the estimated quantitation limit (EQL) for trichloronitromethane is calculated

by: MDL = 3.14*(std dev values), where std dev = the standard deviation of the concentration calculated for the seven replicate spikes. For TCNM the MDL is 3.96 ng/sample (1.32 ng/mL). EQL, defined as 5*MDL, is 19.8 ng/sample (6.60 ng/mL) based on a 3.0 ml extraction volume. Results are reported to three significant figures. Results below EQL but above the MDL are reported as DET (detected) and results less than the MDL are reported as ND (nondetect) or <MDL.

E. Collection and Extraction Efficiency (Recovery)

Trichloronitromethane at a low and high level are spiked on XAD-4 tubes (three at each concentration). The spiked tubes are placed on field samplers with airflows of 100 mLpm for 24 hours. The samples are extracted with DCM and prepared as described in section 5, #6-7. The average percent recovery of trichloronitromethane should be ± 20% of the expected value. The recoveries both for the low and high levels are greater than 80.0%.

F. Storage Stability

Storage stability was set up for a four-week study. Three (3) XAD-4 tubes each were spiked at the low and high-end concentrations. The tubes were stored in the freezer until analyzed. At the low-end concentrations (5 ng/ml), the recovery for the three spikes averaged 106.8 percent, ranging from 103.68 to 113.68 percent. The average percent recovery peaked after fourteen days and was at the lowest after 28 days. At the high end (50 ng/ml), the recovery for the three spikes averaged 90.24 percent, ranging from 88.90 to 92.00 percent. The average percent recovery peaked at fourteen days and was at the lowest at twenty days.

G. Breakthrough

The most recent study for ambient monitoring for 24 hours required a low sample flow rate to meet the requested EQL. A new breakthrough analysis study was conducted. The flow rates tested were 1.0, 0.5, 0.2 and 0.1 Lpm. To meet the EQL and minimize breakthrough possibility, the flow rate for the field sampling was set at 100 mLpm.

H. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

Attachment III

Application Sampling Procedures
For Adsorbent Tubes

Application Sampling Procedures
For Adsorbent Tubes

Overview:

-Collect samples, according to the schedule in Table 1 of this protocol.

-Collect 4 background samples, from each corner sampling position.

-Collect a collocated sample from the downwind site for all sampling periods (except the background period).

-Submit 1 trip blank.

-With the trip blank there should be a total of 152 to 178 samples collected during the study, plus 4 trip spikes (for each chemical, sulfuryl fluoride and chloropicrin).

--All samples are stored either in an ice-chest on dry ice or in a freezer.

-The field log sheet is filled out as the sampling is conducted. All QA samples must be logged onto the log sheet.

-The chain of custody (COC) forms are filled out prior to sample transfer; the originals are transferred with the samples; make and retain copies if desired (not necessary).

Sampling Procedure:

Materials that will be needed to conduct the sampling include:

- -Clip board with log sheets
- -pencils/pens
- -sample labels
- -sample cartridges
- -end caps
- -plastic test tubes
- -zip-lock bags
- -0 to 200 sccpm mass flow meter (MFM) with battery
- -ice chest
- -dry ice

Figure out the route for sampling the 8 locations and try to keep this the same throughout the study.

Preparation and Set-up

On the way to study site, plug the MFM into the battery. It takes the MFMs about 10 minutes to warm up before they can be used. Leave the MFM plugged in until the last sample is taken; unplug when not in use to minimize drop in battery charge. Recharge

the batteries once per week to be on the safe side.

Securely attach one adsorbent sample cartridge to the sampling tree. MAKE SURE THE ARROW ON THE CARTRIDGE IS POINTING TOWARDS THE SAMPLE LINE.

Using the MFM set the flow rate exactly the specified flow rate.

Make sure that the rain/sun cover is pulled down over the sample tube.

Fill out the log sheet, including: log #, start date, time, start counter reading, leak check OK, MFM Serial #, any comments and the weather conditions.

Sample collection and Shipment
Measure (do not re-set) the flow rates at the end of the sampling period with the MFM; leak check the sample lines; record the end data on the log sheet.

Remove the sample cartridge and cap the ends. Attach the sample label like a flag on the secondary end of the tube. Make sure that the label does not cover the glass wool separating the primary and secondary beds in the cartridge.

Place the cartridge in the plastic test tube shipping container.

Place all the samples for each period in a zip-lock freezer storage bag and place on dry ice in a cooler.

Collect a trip blank (TB) by breaking the ends off of a tube, capping and labeling as usual and storing along with the rest of the samples. Log the TB into the log sheet.

Attachment IV

Field Log Sheet

CARTRIDGE FIELD LOG SHEET

Project: Sulfuryl Fluoride/Chloropicrin Fumigation Air Monitoring

Project #: P-03-002 On Flow Set: 100 ±2ccm Off Flow Criteria: 100 ccm ±25%

Log #	Sample Name	Sampler ID Number	Date On / Off	Time On / Off	Counter On / Off	Flow On / Off	True Flow	Comments	Weather K,P,C,F&R On / Off	Initials On / Off

MFM Used #: _____ Slope: _____ Intercept: _____

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog, and R = Rain (any)

Attachment V

General Information
On
Vikane Gas Fumigant

General Information On Methyl Gas Fumigant

INTRODUCTION

Drywood termites and other wood-destroying insects can cause significant damage as they feed on materials containing cellulose found in structures, such as wood, paper, textiles, furnishings, and works of art. Because these insects live most of their life cycle within their food source, the exact distribution and extent of infestation is often difficult to determine. Therefore, localized treatments using physical methods or conventional insecticides may not eradicate all wood-destroying insects infesting a structure. To solve this problem The Dow Chemical Company developed sulfuryl fluoride, the active ingredient of Vikane® gas fumigant, to be used exclusively by professional fumigators (DowElanco 1992).[1]

Research conducted during the development of sulfuryl fluoride demonstrated that this fumigant possesses highly desirable characteristics for the eradication of structure-infesting insects (Derrick et al. 1990). Sulfuryl fluoride is nonflammable, non-corrosive, and does not cause undesirable odors. It quickly penetrates structural materials, is effective against a variety of structural pests, and dissipates rapidly during aeration (Kenaga 1957; Stewart 1957). Since first marketed as Vikane in 1961, sulfuryl fluoride has been used to fumigate more than one million buildings, including museums; historical landmarks, such as the Hearst Castle in California (Pest Control 1977) and the Flagler Museum in Florida (Moon 1981), rare book libraries, government archives, scientific and medical research laboratories, and food-handling facilities.

EFFICACY

Vikane has been demonstrated to reduce oxygen uptake in insect eggs (Outram 1970). Vikane also prevents insects from metabolizing the stored fats they need to maintain a sufficient source of energy for survival by disrupting the glycolysis cycle (Meikle et al. 1963). This metabolic imbalance may delay mortality of insects for several days or more following fumigation (Osbrink et al. 1987). For this reason, insects that have received a lethal exposure to Vikane may still be alive immediately following fumigation.

The activity of Vikane depends on the concentration reaching the target pest and the duration of exposure. Therefore, the dosage of Vikane required for a specific target pest is calculated in "ounce-hours," ounces of Vikane multiplied by hours of exposure. Insect eggs require a higher ounce-hour dosage of Vikane compared to later life stages. Control of the egg stage of social insects, such as termites and ants, is not necessary because newly hatched termites and ants cannot survive without adult care.

Higher dosages required to control eggs of insects, such as wood-boring beetles, can be obtained by increasing the exposure time, increasing the concentration of Vikane, or a combination of both. Fumigators use the Fumiguide® calculation system, which was developed specifically for Vikane, to determine the amount of Vikane required for specific pests and fumigation conditions.

Vikane has also been successfully used since 1961 to control a wide variety of household pests, including cockroaches, clothes moths, rodents, bedbugs and carpet beetles. The eradication of eggs of carpet beetles requires very high dosages of Vikane (Su and Scheffrahn 1990) which are not economically practical. Therefore, two fumigations are required to eradicate carpet beetles using Vikane. The second fumigation is conducted after all beetle larvae have hatched from eggs surviving the first fumigation.

FORMULATION AND PROPERTIES

Sulfuryl fluoride, the active ingredient of Vikane, is a gas at temperatures above -67°F. Vikane is packaged in white cylinders as a liquid under pressure, containing 99.5% sulfuryl fluoride with no other pesticides, solvents or additives. Vikane has a high vapor pressure; it evaporates 20,000 times more readily than mothballs and therefore disperses rapidly from structures.

Vikane does not react with common household furnishings. This is why fumigation with Vikane is an established method used to eradicate pests infesting delicate and rare biological and historical museum artifacts. Food must be protected from exposure to Vikane during fumigation because no residue tolerances have been set for any food product (see PREPARATION). Vikane does not form toxic surface residues in household items, and thus dishes, clothes, and other items do not need to be washed following fumigation with Vikane.

Watering soil around exterior perimeter building foundations is recommended to reduce both loss of fumigant through the soil and exposure of plant roots to Vikane during fumigation. The solubility of sulfuryl fluoride in water is very low, 0.075% by weight at 77°F (Meikle and Stewart 1962).

Vikane is nonflammable and relatively stable; however, it will react to form hydrogen fluoride at extremely high temperatures exceeding 752°F. This acid can etch metals, glass, ceramic tile, or china near the heat source. Thus, prior to structural fumigation, all open flames and glowing heat filaments are turned off or disconnected.

Vikane is odorless at concentrations used to fumigate structures and is not irritating as a gas to the eyes or skin. For these reasons, a trace amount of the warning agent, chloropicrin, is introduced in the structure prior to fumigation to warn people and animals that the structure is being fumigated. Chloropicrin acts as a warning by causing irritation of the eyes, tears, discomfort, and has a noticeable disagreeable pungent odor even at very low concentrations, less than 1 part per million (ppm).

Chloropicrin diffuses from structures more slowly than Vikane. Thus, occupants may experience some eye irritation after all of the Vikane has aerated from the structure. The fumigator should be contacted to take remedial measures if this occurs. A trained fumigator will use an approved clearance device, such as an Interscan[1] or Miran[2], to determine that the concentration of Vikane within the structure is 5 ppm or less prior to allowing anyone to reoccupy the structure.

[1]DowElanco is now known as Dow AgroSciences LLC

FUMIGATION PREPARATION

The label for Vikane requires that the following preparations be completed prior to releasing the fumigant into the structure.

1. All animals (including fish) and plants must be removed from the structure to be fumigated.
2. Mattresses and pillows completely enveloped in water-proof covers (not including waterbeds) must be removed from the area to be fumigated if the covers can not be removed. The water-proof covers restrict dispersion of fumigant during aeration.
3. All flames such as pilot lights and electric heating elements must be turned off for reasons previously described[3].
4. The following should be opened prior to fumigation: internal doors, internal openings to attics and sub-areas, storage chests, cabinets, drawers, closets, and appliances such as washers, dryers and ovens. In tarpaulin fumigations, operable windows are opened. These procedures assist in rapid dispersion of Vikane during fumigation and aeration.
5. Food, feed, drugs and medicinals, including items in refrigerators and freezers, must be removed from the fumigation site or sealed in highly resistant containers such as glass, metal or plastic or enclosed in special bags according to label directions.

   This is required because exposure of unprotected foodstuffs to Vikane may result in the formation of temporary sulfuryl fluoride residues and permanent fluoride residues. However, experimental exposure of food commodities protected in two nylon bags to 10x dosages of Vikane resulted in no detectable sulfuryl fluoride or added fluoride residues. Two nylon bags reduced the exposure of protected foodstuffs to Vikane by 99.99% (Scheffrahn et al. 1990). Excessive exposure to fluoride can have toxicologically significant effects, although long-term human intake of water containing up to 1 mg/l (1 ppm) fluoride is generally considered not to result in adverse effects. (National Research Council 1977).

FUMIGANT DOSAGE DETERMINATION

Because of a multitude of structural, environmental, and fumigation variations, there are no two fumigation jobs that are identical. The required dosage of Vikane is influenced by the temperature at the site of the pest, the length of the exposure period and the susceptibility of the pest to be controlled. Consequently, the dosages vary, but the typical single family home fumigation involves the use of 6-16 ounces/1000 cubic ft (1440-3850 ppm). The length of the exposure period is critical to accumulate sufficient ounce-hours[4] required for the temperature at the site of the pest. The ounce-hours required to control target insect pests have been determined from laboratory and field testing.

RELEASING VIKANE

Five to ten minutes prior to introducing Vikane into the structure, the fumigator will place a warning agent, chloropicrin, in the structure. This warning agent is required to warn any person or animal that may have entered the structure after the final inspection by the fumigator. Once the building is determined to be cleared of all people and animals, the fumigator will release the Vikane into the structure.

Vikane is packaged in 125 lb. cylinders that fumigators transport on their vehicles. The fumigator introduces Vikane through tubing into the air stream of a fan that helps disperse the fumigant throughout the structure. Once the appropriate amount of Vikane is introduced, the fumigator turns off the cylinder valve and removes the tubing from the cylinder.

FUMIGATION PERIOD

Vikane is usually held in the structure for approximately 16-30 hours. Fumigation time is dependent upon the factors mentioned previously[5]. When the fumigation exposure period is complete, the fumigator will return to the structure to conduct the aeration procedure.

AERATION

Aeration is the final step of a fumigation. Aeration involves proper ventilation and clearance of Vikane and the warning agent, chloropicrin, from a structure.

The Occupational, Safety & Health Administration (OSHA) established a Permissible Exposure Level (PEL) of 5 parts per million (ppm) for Vikane. A PEL is the Time Weighted Average (TWA) exposure to which it is believed that most members of a healthy working population can be exposed 40 hours/week for a working lifetime.

The fumigator must aerate a structure so that the concentration of Vikane in the air is 5 ppm or less prior to allowing reentry. This 5 ppm PEL is substantially lower than the level that may affect people and pets following even long-term exposure.

Unlike liquid and solid insecticides, Vikane is a gas possessing a very high vapor pressure (potential to escape from an area) and low boiling point (it is a gas above -67°F). During aeration of the fumigated structure, Vikane will quickly diffuse from high concentrations within a structure to the outside air where it rapidly dissipates to nondetectable levels.

Degassing is the process of fumigant diffusing out of materials when the concentration of gas is less around the object than within the object. Required aeration procedures allow the fumigant time to diffuse from structural voids and household materials and be ventilated out of the structure. The fumigator will use powerful fans and open cabinets, doors, and windows to speed the process of aeration.

Many structures have been tested by university researchers and DowElanco[1] scientists with the goal of developing new aeration procedures. The aeration procedures have been vigorously tested to ensure that even under poor ventilation conditions concentrations of Vikane will not increase after occupants return.

Only specially trained and state-licensed/certified professionals can determine that a structure can be reoccupied. Unique equipment, such as the Interscan and Miran, must be used to test the concentrations of Vikane within structures. The Interscan is specially designed to detect levels of Vikane down to 1 ppm.

[1]DowElanco is now known as Dow AgroSciences LLC

VIKANE AND THE ENVIRONMENT

When Vikane is aerated from a structure it rapidly dissipates into the atmosphere because of its high vapor pressure. Vikane is broken down mainly through hydrolysis to release fluoride and fluorosulphate ions. Ultraviolet radiation and reactions with solid particles in the atmosphere may also catalyze the breakdown of Vikane.

The relatively small amounts of Vikane released are calculated to have virtually no impact on global atmosphere/environment. Sulfuryl fluoride is fully oxidized, and thus is not expected to interact or contribute to local ozone formation (such as Los Angeles smog) because of its low reactivity in the atmosphere. The relative contribution of Vikane to acid rain is infinitely small compared to the massive amount of sulfur released into the atmosphere from industry. Vikane contains no chlorine or bromine and thus can not react to deplete stratospheric ozone by the known mechanisms (Bailey 1992).

TOXICOLOGY OF VIKANE

Mode of Action, Symptoms of Overexposure

The severity of toxicological effects is dependent on the exposure concentration and exposure duration. The mode of action by which Vikane produces its toxicity in humans depends on the exposure concentration. In general, the effects of overexposure to high concentrations are central nervous system depression and respiratory irritation followed by pulmonary edema, which is the accumulation of fluids in the lungs and can result in death. Humans exposed to high concentrations of Vikane may expect to experience symptoms similar to drunkenness. Speech and movements may be slowed, and fingers, hands, and toes may become numb.

Animal studies may indicate that some sulfuryl fluoride is converted to fluoride ion in the body. Chronic exposure may result in fluoride binding to the teeth and bones, causing fluorosis, which is manifested as mottled teeth.

Applicators who work with Vikane can have their urine checked for fluoride. However, high fluoride levels in the urine could be due to chemicals other than sulfuryl fluoride, for example, fluorides in drinking water, fluorinated tooth paste, and some medicines.

Time to Incapacitation

Another factor to be considered in the safe use of Vikane is the length of time in which a person might have "escape capability" during exposure to high levels of Vikane. Researchers have investigated this by determining the length of time that rats are able to maintain coordinated activity when exposed to very high concentrations of Vikane. The time to incapacitation of laboratory rats for various exposure concentrations were (Nitschke et al. 1986):

42 minutes at 4,000 ppm
16 minutes at 10,000 ppm
10 minutes at 20,000 ppm
6 minutes at 40,000 ppm

Exposures were terminated when incapacitation occurred. All rats died or were moribund within 3 hours following the end of exposure. Therefore, the above exposures can be considered to produce 100% mortality in rats. For comparison, typical initial concentrations in single family homes are 1440-3850 ppm and must be reduced to 5 ppm or less before humans can enter dwellings without respiratory protection.

[1]Manufactured by Interscan Corporation, Chatsworth, CA 91311

[2]Manufactured by The Foxboro Company, East Bridgewater, MA 02333

[3]See the section on FORMULATION AND PROPERTIES

[4]See the section on EFFICACY

[5]See the section on Vikane FUMIGANT DOSAGE DETERMINATION

Repeated Exposure Toxicity Studies

Rats, rabbits, and dogs have been studied following daily repeated exposures to Vikane. Exposures of 30 ppm 6 hours/day, 5 days/week for 13 weeks had no effects on rats or rabbits, while dogs showed no effects from 100 ppm in a similar exposure regimen. Rats exposed to 300 ppm had decreased body weights, mottled teeth, and microscopic evidence of brain and kidney injury and respiratory irritation. Rabbits exposed to 100 or 300 ppm showed decreased body weights and microscopic changes in brain and nasal tissues. Dogs exposed to 200 ppm showed nervous system effects, including microscopic changes in the brain.

Studies For Effects On Reproduction And Development Of Offspring

The results of the studies described here indicate that Vikane is not likely to have any effects on reproduction or development of offspring. Groups of pregnant rats and rabbits were exposed to Vikane at three different concentrations: 25, 75, or 225 ppm for 6 hours/day during the majority of the gestation period. Although the highest level of 225 ppm was toxic to the maternal animals (as would be expected), there was no evidence that Vikane was teratogenic (causing birth defects in offspring of exposed females). The only effects on the fetus were reduced body weights in the rabbits at the highest level, probably associated with the maternal weight loss. In a reproduction study, male and female rats were exposed to concentrations of 5, 20, or 150 ppm throughout two generations.

The highest level of 150 ppm was toxic to the parent animals, producing effects similar to those seen in the 13-week study described in the preceding section. Parent animals exposed to 5 ppm were without evidence of effects. Decreased weights of the offspring were observed at 150 ppm that may have been secondary to decreased maternal growth. The only effect observed at 20 ppm was mild lung irritation in parental rats, with no evidence of toxicity in offspring. There were no effects on reproductive performance in any exposure group.

Carcinogenicity And Mutagenicity Studies

Vikane has been tested in a battery of mutagenicity tests that serve as a screen for identifying chemicals that affect genetic mechanisms. All test results have been negative, indicating that Vikane is not mutagenic in standard testing. Lifetime studies in which rats and mice were exposed to Vikane to assess whether or not the chemical has potential to cause cancer were also negative.

Neurological Effects

Rats exposed for 6 hours a day for 2 days to 100 ppm and 300 ppm showed no signs of neurotoxicity.

Other Routes Of Exposure To Vikane

Inhalation is the primary route of exposure to Vikane. Ingestion is highly unlikely since the material is a gas at temperatures higher than -67°F. Laboratory animals maintained for 66 days on feed directly fumigated at 2 lb/1000 cubic ft (7700 ppm) showed no adverse effects. Typical structural fumigation concentrations are 1 lb/1000 cubic ft (3850 ppm) or less. Feed exposed to abnormally high application rates (10-200 lb/1000 cubic ft; 38,500 to 770,000 ppm) and fed to test animals caused decreased body weight gains and fluorosis of the teeth. The gas is not absorbed through the skin in acutely toxic amounts; rats exposed dermally for 4 hours to concentrations of 9599 ppm did not show evidence of toxicity.

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[1]DowElanco is now known as Dow AgroSciences LLC.

Attachment VI

UPDATED METHOD VALIDATION DATA FOR ANALYSIS OF SULFURYL FLUORIDE

Air Resources Board

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Terry Tamminen
Agency Secretary

Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Webster Tasat, Manager
Operations Planning and Assessment Section

FROM: Russell Grace, Manager //s//
Special Analysis Section

DATE: February 27, 2004

SUBJECT: CORRECTED METHOD VALIDATION DATA FOR ANALYSIS OF SULFURYL FLUORIDE

The Special Analysis Section recently released an update to the method validation data through a memo dated February 20, 2004. Table 1, Method Detection Limit, contained data from the original method development activities but instead should have included data generated since the method has been modified. The attached table contains the current data generated to determine the method detection limit (MDL) and the estimated quantitation limit (EQL). Please disregard the data in Table 1 from the February 20, 2004 memo. All other data presented in that memo (reproducibility, extraction efficiency, collection efficiency, storage stability and breakthrough) are current and valid.

All of the method development procedures summarized in the standard operating procedure (SOP) for sulfuryl fluoride, dated January 14, 2004, are correct.

If you have any questions, please contact Mr. Jim Omand at 324-1969 or me at 322-0223.

Attachment
cc: Michael Poore
T. E. Houston
Jim Omand
Michael Orbanosky
Kevin Mongar

TABLE 1

METHOD DETECTION LIMIT/ESTIMATED QUANTITATION LIMIT DETERMINATION

800/200 coconut charcoal tubes

Analyzed 6/18/03		Analyzed 6/20/03	
Sample #	µg F^-/ml	Sample #	µg F^-/ml
1	0.118	1	0.084
2	0.164	2	0.132
3	0.126	3	0.116
4	0.128	4	0.113
5	0.162	5	0.150
6	0.084	6	0.076
7	0.136	7	0.130
N=	7		7
Mean=	0.131		0.114
SD=	0.027		0.027
MDL (3.14*SD)=	0.086		0.083
EQL (5*MDL)=	0.429		0.417

MDL (instrument) = 0.0859µg F^-/ml x 10 ml = 0.859 µg F^-/sample
EQL (instrument) = 0.429 µg F^-/ml x 10 ml = 4.29 µg F^-/sample

24-hour sample volume = 50ml/min x 60 min/hr x 24 hr = 72000 ml or .072 m^3

MDL = 0.859 µg/0.072 m^3 = 12 µg/m^3 x 102/38 = 32 µg/m^3 sulfuryl fluoride (24 hour sample)
EQL = 5 x 32 µg/m^3 = 160 µg/m^3 sulfuryl fluoride (24 hour sample)

Air Resources Board

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Terry Tamminen
Agency Secretary

Arnold Schwarzenegger
Governor

MEMORANDUM

TO: Webster Tasat, Manager
Operations Planning and Assessment Section

FROM: Russell Grace, Manager
Special Analysis Section

DATE: February 20, 2004

SUBJECT: UPDATED METHOD VALIDATION DATA FOR ANALYSIS OF SULFURYL FLUORIDE

One of the responsibilities of the Special Analysis Section in providing laboratory support for the pesticide air monitoring program is laboratory analytical method development. By way of this memo, I am providing you with an update to the method validation data generated in the development of the sulfuryl fluoride analytical method. The attached tables contain the currently available data generated to determine the method detection limit (MDL), estimated quantitation limit (EQL), reproducibility, extraction efficiency, sampling efficiency and breakthrough, and storage stability.

All of the method development procedures were summarized in the standard operating procedure (SOP) for sulfuryl fluoride, dated January 14, 2004. This SOP has been provided to you.

If you have any questions, please contact Mr. Jim Omand at 324-1969 or me at 322-0223.

Attachment
cc: Michael Poore
T. E. Houston
Jim Omand
Michael Orbanosky
Kevin Mongar

TABLE 1

METHOD DETECTION LIMIT
fluoride

	µg/ml
1	0.273
2	0.251
3	0.254
4	0.256
5	0.246
6	0.255
7	0.254
Average	**0.256**
Standard Deviation	**0.00838**
MDL (3.14*sd)	**0.026**
EQL	**0.13**

TABLE 2

REPRODUCIBILITY STUDY
(800/200 mg coconut charcoal tubes)

µg sulfuryl fluoride

#	Low Level	Med Level	High Level
1	10.04	45.74	88.79
2	10.90	44.72	93.97
3	12.64	47.03	94.35
4	13.23	46.65	90.70
5	10.52	45.36	91.16
Average	**11.47**	**45.90**	**91.79**
Std. Deviation	**1.39**	**0.94**	**2.34**
Coef. Variation	**12.1**	**2.1**	**2.5**

TABLE 3

EXTRACTION EFFICIENCY
(800/200 mg coconut charcoal tubes)

µg sulfuryl fluoride

#	20.6 µg spike		55.1 µg spike	
	µg recovered	% recovery	µg recovered	% recovery
1	17.31	84	51.86	94
2	17.26	84	48.45	88
3	16.96	82	47.83	87
Average	**17.18**	**83**	**49.38**	**90**
Std. Deviation	**0.19**		**2.17**	
Coeff. Var. %	**1.1**		**4.4**	

TABLE 4

SAMPLING EFFICIENCY AND BREAKTHROUGH
(800/200 mg coconut charcoal tubes)
spike value = 330 µg sulfuryl fluoride
sampling rate = 50 ml/min

sampling date*	front bed		rear bed		Total
	µg SF	% recovery	µg SF	% recovery	% recovery
5/20/2003	274	83.0	DET	NA	83.0
5/21/2003	300	90.9	DET	NA	90.9
6/2/2003	265	80.3	64	19.4	99.7
6/17/2003	234	70.9	30	9.1	80.0
6/17/2003	259	78.5	32	9.7	88.2

spike value = 123 µg sulfuryl fluoride
sampling rate = 50 ml/min

sampling date*	front bed		rear bed		Total
	µg SF	% recovery	µg SF	% recovery	% recovery
1/6/04	107	87.0	det	NA	87.0
1/7/04 #1	107	87.0	det	NA	87.0
1/7/04 #2	122**	93.1***	det	NA	93.1

* samples were collected @13th & T air monitoring station using ambient air as make-up for 3 hours
** sample was collected for an extra 12 minutes (target value 131 µg).
*** % recovery value is corrected for an additional 12 minute sampling time.

16-hour sample @ 50 ml/min. using zero air as make-up in lab hood: target value 1758 µg

sampling date	primary tube		secondary tube		Total
	front bed	rear bed	front bed	rear bed	% recovery
6/10/2003	1632 (92.8%)	DET	DET	DET	92.8

TABLE 5

STORAGE STABILITY

Storage Time	7.66 µg		20.4 µg	
	µg	% recovery	µg	% recovery
1 day	8.01	105	21.07	103
10 days	7.66	100	19.36	95
19 days	7.85	102	19.02	93
49 days	7.38	96	19.68	96
55 days	8.20	107	22.00	108

(800/200 mg coconut charcoal tubes)
spike samples held in freezer for 6 weeks
µg sulfuryl fluoride

#	20.6 µg spike		55.1 µg spike	
	µg recovered	% recovery	µg recovered	% recovery
1	18.71	91	48.18	87
2	18.39	89	48.80	89
3	19.38	94	49.77	90
Average	**18.83**	**91**	**48.92**	**89**
Std. Deviation	**0.51**		**0.80**	
Coef. Var. %	**2.7**		**1.6**	

APPENDIX II

LABORATORY REPORT FOR
SULFURYL FLUORIDE

California Environmental Protection Agency

Air Resources Board

Sulfuryl Fluoride (Vikane) Analytical Results for Application Air Monitoring Samples in Placer County

DATE: October 2004

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Reviewed and Approved by

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Special Analysis Section

Project Number: P03-002

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1.0 INTRODUCTION

The Department of Pesticide Regulation (DPR) requested the Air Resources Board (ARB) to conduct application air monitoring for sulfuryl fluoride (Vikane). This report covers the analytical and quality assurance results for a Vikane application occurring over a six (6) day period in Placer County. DPR requested an estimated quantitation limit (EQL) of 30 µg/m^3 for sulfuryl fluoride. The EQL achieved during this project was 160 µg/m^3

2.0 METHOD DEVELOPMENT

2.1 Overview

The method uses coconut charcoal cartridges for application air sampling. Exposed sample cartridges are stored at or below four (4) degrees centigrade (°C) before extraction. Sample cartridges are extracted with ten (10) milliliters (ml) of 40 millimolar (mM) sodium hydroxide (NaOH) and desorbed in an ultrasonic bath. Sample extracts are analyzed using an ion chromatograph equipped with a conductivity detector. Sulfuryl fluoride is measured as fluoride ion (F^-). Sample analysis and quantitation used the external standard calibration method. The estimated quantitation level for this method, based on 0.072 cubic meters (m^3) of air collected, and a final extract volume of ten (10) ml, is 160 µg/m^3.

2.2 Calibration Curve

Laboratory staff used standard concentrations of approximately 0.1, 0.2, 0.4, 0.8, 1.6, and 3.2 µg/ml F^- to produce a six (6) point calibration curve. All calibration curves used for quantitation had an r^2 (correlation coefficient) greater than or equal to 0.995. Laboratory staff performed calibrations at the beginning of each analytical batch.

2.3 Method Detection Limit (MDL)

The MDL calculation follows the United States Environmental Protection Agency procedures for calculating MDL's. Using the analysis of seven low-level matrix spikes (0.2 µg/ml F^-), the MDL and EQL for a ten (10) ml extract is calculated as follows:

s = the standard deviation of the concentration calculated for the seven replicate spikes. For sulfuryl fluoride: s = 0.027 µg/ml (F^-)

MDL = (3.14) x (s) = (3.14) x (0.027) = 0.086 µg/ml (F^-)
EQL = (5) x (MDL) = (5) x (0.086) = 0.43 µg/ml (F^-)
EQL = 0.43 µg /ml x 102/38 = 1.15 µg/ml sulfuryl fluoride
EQL = 1.15 µg/ml x 10ml = 11.5 µg sulfuryl fluoride / sample

Staff report results above the EQL to three (3) significant figures. Results below the EQL but greater than or equal to the MDL are reported as detected (DET). Results less than MDL are reported as <MDL.

2.4 Method Development

Staff performed studies on 400/200 charcoal tubes for reproducibility, collection and extraction efficiency, storage stability and breakthrough. These studies were reported to the MLD Operations Planning and Assessment Section on July 24, 2002 in a memorandum " Method Validation Data for Analysis of Sulfuryl Fluoride."

Staff performed additional studies on 800/200 mg charcoal tubes at a sample collection rate of 50 milliliters per minute (mLPM). The results for these studies were reported in a memorandum to the MLD Operations Planning and Assessment Section on February 20, 2004 and February 27, 2004.

3.0 SULFURYL FLUORIDE APPLICATION AIR MONITORING RESULTS

The laboratory received 154 samples which included one (1) trip blank, and four (4) trip spikes on July 1, 2004, and two (2) ARB-Sacramento spikes that were collected for this project. Table 1 presents the analytical results for the application samples by sampler location.

4.0 ANALYTICAL QUALITY CONTROL SAMPLES

4.1 System Blanks

Laboratory staff analyzes a system blank with each analytical batch. Staff defines the analytical batch as all the samples extracted in the same group. The system blank is run to insure the solvent and instrument do not contribute interferences to the analytical results. All system blanks were less than the MDL.

4.2 Method Blanks

Laboratory staff analyzed a method blank with each analytical batch. This is a charcoal

cartridge prepared and analyzed as described for the application samples. Laboratory staff analyzed eleven (11) method blanks during this project. All method blank results were DET with the exception of the method blanks analyzed on 7/14/04 and 7/27/04 which were <MDL.

4.3 Laboratory Control Samples (LCS)

Laboratory staff analyzed two LCS samples with each analytical batch. A LCS is a charcoal cartridge spiked with 32.9 ppm +/- 2% sulfuryl fluoride gas (certified by Scott-Marrin). The LCS samples are extracted and analyzed as described for the samples. The low level LCS was spiked with 150 ml of certified gas (20.55 mg of sulfuryl fluoride). The low level spike recoveries averaged 21.1 mg (103%) with a coefficient of variation (CV) of 9.5%. The high level LCS was spiked with 400 ml of certified gas (54.8 mg of sulfuryl fluoride). The high level spike recoveries averaged 52.3 mg (96%) with a CV of 8.1%. All LCS sample results were within three standard deviations of their respective sample means.

4.4 Continuing Calibration Verification Standards (CCV)

Laboratory staff analyzed a CCV after every tenth (10) sample and at the end of each analytical batch. The CCV must be within $\pm$ 10 % of the expected value. If any of the CCVs are outside this limit, the affected samples are re-analyzed. The CCV target value for this project was 3.2 µg/ml. All CCV's were within $\pm$ 10 % of the expected value.

4.5 Laboratory Duplicates

No laboratory duplicates were run with this project.

5.0 LABORATORY, TRIP AND FIELD SPIKES AND TRIP BLANKS

During the application project, four (4) trip and (2) ARB-Sacramento spikes along with four (4) laboratory spikes and one (1) trip blank were analyzed. Laboratory staff prepared trip and laboratory spikes at 55.2 µg /sample of sulfuryl fluoride.

5.1 Laboratory Spikes

Table 2 presents the results of the laboratory spikes. The average sulfuryl fluoride recovery was 55.0 µg /sample (100%) with a standard deviation of 3.79 µg /sample and a coefficient of variation (CV) of 6.9%.

5.2 Trip Spikes

Table 2 presents the results of the trip spikes. The average recovery for sulfuryl fluoride was 52.2 µg /sample (94%) with a standard deviation of 2.10 µg /sample and a CV of 4.0%.

5.3 Field Spikes

Field spikes were not collected for this project, however, two ARB-Sacramento spikes were collected using a "dynamic" collection technique. The spikes were collected on 6/30/2004 and 7/1/2004 in the breezeway at the MLD building at 13th & T Street in Sacramento. The expected value for these samples was 395 µg /sample. The spike analytical results are: 331 µg /sample (84%) and 324 µg /sample (82%), respectively.

5.4 Trip Blanks

One (1) trip blank, with result of DET, was received during this project.

6.0 DISCUSSION

In order to minimize sample breakthrough Version 2 of the SOP "Standard Operating Procedure for the Determination of Sulfuryl Fluoride Measured as Fluoride by Ion Chromatography" was developed for this project. Version 2 uses 800/200 charcoal tubes instead of 400/200 tubes and uses a sampling rate of fifty (50) milliliters per minute (mLPM) instead of one liter per minute (LPM). Additional method verification was done to show that sample breakthrough is minimal using Version 2. The additional studies included a dynamic sampling technique to evaluate sample breakthrough.

ARB-Sacramento spikes for the current project were collected using a dynamic technique. This technique included spiking a known amount of sulfuryl fluoride into an ambient air sample stream for sample collection. These spikes were collected in the breezeway at the MLD building at 13th and T Street in Sacramento. The 24-hour spikes collected on 6/30/04 and 7/1/04 showed sample recoveries of 84 and 82%, respectively.

Samples collected during the current project were evaluated for sample breakthrough. The samples from period five (sample # 67-98) were collected using two charcoal tubes in series. Staff analyzed the primary resin beds of the front and back tubes for all samples collected during the 5th sampling period. None of the primary beds from the back tubes had a quantifiable amount of sulfuryl fluoride. Staff analyzed the secondary beds of the front tubes of some period five samples which had quantifiable sulfuryl fluoride in the primary bed. None of these secondary beds had quantifiable amounts of sulfuryl fluoride. In addition, the secondary beds of sample numbers 28, 41, 55 and 56 were analyzed and no quantifiable amount of sulfuryl fluoride was detected in any of these samples. These results indicate that sample breakthrough was not a significant issue during the current project.

Because all system blanks were <MDL and most extraction blanks were DET it seems probable that the charcoal collection tubes contain a small amount of fluoride. Blank values were not subtracted from the monitoring data.

DPR requested an EQL of 30 µg/m^3 but MLD was only able to achieve an EQL of

160 µg/ m^3 using SOP Version 2. The high analytical EQL may be due to the larger primary sampling bed (800 mg) and the lower sampling rate of 50 ml/min, as compared to Version 1 of the SOP.

The extra vent cycle sample XNE-SF-5B (#96) was a back tube (primary resin bed) that had 15.46 µg of sulfuryl fluoride (EQL=11.5 µg). The front tube primary resin bed for this sample (XNE-SF-5F, #95) was measured as DET. This can be explained by contamination or sample mix-up. It does not represent sample breakthrough.

Table 1: Structural Application Air Monitoring Results for Sulfuryl Fluoride

(results in µg/sample of sulfuryl fluoride)

Site	Log Number	Sample ID	Date Received	Front Bed (µg/sample)	Rear Bed (µg/sample)
East Inner	015	EI-SF-1	7/1/04	1.03E+02	NA
	030	EI-SF-2	7/1/04	2.34E+01	NA
	044	EI-SF-3	7/4/04	8.12E+01	NA
	058	EI-SF-4	7/4/04	2.01E+01	NA
	077	EI-SF-5F	7/4/04	1.03E+02	DET
	078	EI-SF-5B	7/4/04	DET	DET
	104	EI-SF-6	7/4/04	1.23E+01	NA
	118	EI-SF-7	7/4/04	DET	NA
	132	EI-SF-8	7/4/04	DET	NA
	146	EI-SF-9	7/4/04	<MDL	NA
East Outer	022	EO-SF-1	7/1/04	DET	NA
	036	EO-SF-2	7/1/04	<MDL	NA
	051	EO-SF-3	7/4/04	1.53E+01	NA
	065	EO-SF-4	7/4/04	DET	NA
	091	EO-SF-5F	7/4/04	2.75E+01	DET
	092	EO-SF-5B	7/4/04	<MDL	DET
	111	EO-SF-6	7/4/04	DET	NA
	125	EO-SF-7	7/4/04	DET	NA
	139	EO-SF-8	7/4/04	DET	NA
	153	EO-SF-9	7/4/04	<MDL	NA

Site	Log Number	Sample ID	Date Received	Front Bed (µ/sample)	Rear Bed (µg/sample)
North	012	N-SF-1	7/1/04	6.29E+01	NA
	013	N-SF-1C	7/1/04	6.47E+01	NA
	027	N-SF-2	7/1/04	1.16E+02	NA
	028	N-SF-2C	7/1/04	1.38E+02	DET
	041	N-SF-3C	7/4/04	9.39E+01	DET
	042	N-SF-3	7/4/04	7.95E+01	NA
	055	N-SF-4C	7/4/04	1.22E+02	DET
	056	N-SF-4	7/4/04	1.07E+02	DET
	073	N-SF-5F	7/4/04	5.20E+01	NA
	071	N-SF-5CF	7/4/04	5.49E+01	DET
	074	N-SF-5B	7/4/04	DET	NA
	072	N-SF-5CB	7/4/04	DET	NA
	102	N-SF-6	7/4/04	DET	NA
	101	N-SF-6C	7/4/04	DET	NA
	116	N-SF-7	7/4/04	DET	NA
	115	N-SF-7C	7/4/04	DET	NA
	130	N-SF-8	7/4/04	DET	NA
	129	N-SF-8C	7/4/04	DET	NA
	144	N-SF-9	7/4/04	DET	NA
	143	N-SF-9C	7/4/04	DET	NA
Northeast Inner	014	NEI-SF-1	7/1/04	3.27E+01	NA
	029	NEI-SF-2	7/1/04	DET	NA
	043	NEI-SF-3	7/4/04	2.52E+01	NA
	057	NEI-SF-4	7/4/04	1.33E+01	NA
	075	NEI-SF-5F	7/4/04	3.52E+01	DET
	076	NEI-SF-5B	7/4/04	DET	DET
	103	NEI-SF-6	7/4/04	DET	NA
	117	NEI-SF-7	7/4/04	DET	NA
	131	NEI-SF-8	7/4/04	DET	NA
	145	NEI-SF-9	7/4/04	<MLD	NA
	006	NEI-SF-B	7/1/04	DET	NA

Site	Log Number	Sample ID	Date Received	Front Bed (µg/sample)	Rear Bed (µg/sample)
Northeast outer	021	NEO-SF-1	7/1/04	1.75E+01	NA
	035	NEO-SF-2	7/1/04	DET	NA
	050	NEO-SF-3	7/4/04	1.65E+01	NA
	064	NEO-SF-4	7/4/04	DET	NA
	089	NEO-SF-5F	7/4/04	2.29E+01	DET
	090	NEO-SF-5B	7/4/04	DET	DET
	110	NEO-SF-6	7/4/04	DET	NA
	124	NEO-SF-7	7/4/04	DET	NA
	138	NEO-SF-8	7/4/04	DET	NA
	152	NEO-SF-9	7/4/04	<MDL	NA
Northwest Inner	011	NWI-SF-1	7/1/04	DET	NA
	026	NWI-SF-2	7/1/04	4.51E+01	NA
	040	NWI-SF-3	7/4/04	DET	NA
	054	NWI-SF-4	7/4/04	1.80E+01	NA
	069	NWI-SF-5F	7/4/04	1.74E+01	NA
	070	NWI-SF-5B	7/4/04	DET	NA
	100	NWI-SF-6	7/4/04	DET	NA
	114	NWI-SF-7	7/4/04	DET	NA
	128	NWI-SF-8	7/4/04	DET	NA
	142	NWI-SF-9	7/4/04	DET	NA
	005	NWI-SF-B	7/1/04	DET	NA
Northwest Outer	020	NWO-SF-1	7/1/04	DET	NA
	034	NWO-SF-2	7/1/04	1.54E+01	NA
	049	NWO-SF-3	7/4/04	DET	NA
	063	NWO-SF-4	7/4/04	DET	NA
	087	NWO-SF-5F	7/4/04	DET	NA
	088	NWO-SF-5B	7/4/04	DET	NA
	109	NWO-SF-6	7/4/04	DET	NA
	123	NWO-SF-7	7/4/04	DET	NA
	137	NWO-SF-8	7/4/04	DET	NA
	151	NWO-SF-9	7/4/04	DET	NA

Site	Log Number	Sample ID	Date Received	Front Bed (µg/sample)	Rear Bed (µg/sample)
Southeast	016	SE-SF-1	7/1/04	DET	NA
	031	SE-SF-2	7/1/04	DET	NA
	045	SE-SF-3	7/4/04	DET	NA
	059	SE-SF-4	7/4/04	DET	NA
	079	SE-SF-5F	7/4/04	DET	NA
	080	SE-SF-5B	7/4/04	DET	NA
	105	SE-SF-6	7/4/04	DET	NA
	119	SE-SF-7	7/4/04	DET	NA
	133	SE-SF-8	7/4/04	DET	NA
	147	SE-SF-9	7/4/04	DET	NA
	007	SE-SF-B	7/1/04	DET	NA
South Inner	017	SI-SF-1	7/1/04	DET	NA
	032	SI-SF-2	7/1/04	DET	NA
	046	SI-SF-3	7/4/04	DET	NA
	060	SI-SF-4	7/4/04	DET	NA
	081	SI-SF-5F	7/4/04	DET	NA
	082	SI-SF-5B	7/4/04	DET	NA
	106	SI-SF-6	7/4/04	DET	NA
	120	SI-SF-7	7/4/04	<MDL	NA
	134	SI-SF-8	7/4/04	DET	NA
	148	SI-SF-9	7/4/04	DET	NA
South Outer	023	SO-SF-1	7/1/04	DET	NA
	037	SO-SF-2	7/1/04	DET	NA
	052	SO-SF-3	7/4/04	DET	NA
	066	SO-SF-4	7/4/04	DET	NA
	093	SO-SF-5F	7/4/04	DET	NA
	094	SO-SF-5B	7/4/04	DET	NA
	112	SO-SF-6	7/4/04	DET	NA
	126	SO-SF-7	7/4/04	DET	NA
	140	SO-SF-8	7/4/04	DET	NA
	154	SO-SF-9	7/4/04	DET	NA

Site	Log Number	Sample ID	Date Received	Front Bed (µg/sample)	Rear Bed (µg/sample)
Southwest Outer	024	SWO-SF-1	7/1/04	DET	NA
	038	SWO-SF-2	7/1/04	DET	NA
	048	SWO-SF-3	7/4/04	DET	NA
	062	SWO-SF-4	7/4/04	DET	NA
	085	SWO-SF-5F	7/4/04	DET	NA
	086	SW0-SF-5B	7/4/04	DET	NA
	108	SWO-SF-6	7/4/04	DET	NA
	122	SWO-SF-7	7/4/04	DET	NA
	136	SWO-SF-8	7/4/04	DET	NA
	150	SWO-SF-9	7/4/04	DET	NA
Southwest Inner	018	SWI-SF-1	7/1/04	DET	NA
	033	SWI-SF-2	7/1/04	DET	NA
	047	SWI-SF-3	7/4/04	DET	NA
	061	SWI-SF-4	7/4/04	DET	NA
	083	SWI-SF-5F	7/4/04	DET	NA
	084	SWI-SF-5B	7/4/04	DET	NA
	107	SWI-SF-6	7/4/04	DET	NA
	121	SWI-SF-7	7/4/04	DET	NA
	135	SWI-SF-8	7/4/04	DET	NA
	149	SWI-SF-9	7/4/04	DET	NA
	008	SWI-SF-B	7/1/04	DET	NA
West	010	W-SF-1	7/1/04	DET	NA
	025	W-SF-2	7/1/04	2.23E+01	NA
	039	W-SF-3	7/4/04	DET	NA
	053	W-SF-4	7/4/04	DET	NA
	067	W-SF-5F	7/4/04	2.35E+01	NA
	068	W-SF-5B	7/4/04	DET	NA
	099	W-SF-6	7/4/04	DET	NA
	113	W-SF-7	7/4/04	DET	NA
	127	W-SF-8	7/4/04	DET	NA
	141	W-SF-9	7/4/04	DET	NA

Site	Log Number	Sample ID	Date Received	Front Bed (µg/sample)	Rear Bed (µg/sample)
Vent Cycle Extra	95	XNE-SF-5F	7/4/04	DET	NA
	96	XNE-SF-5B	7/4/04	1.55E+01	NA
	97	XNW-SF-5F	7/4/04	DET	NA
	98	XNW-SF-5B	7/4/04	DET	NA

Table 1 Notes: Application Monitoring Results

If analytical result is ≥ MDL and < EQL it is reported in the table as detected (DET). Levels at or above the EQL are reported as the actual measured value and are reported to three significant figures.

MDL = 2.32 µg sulfuryl fluoride / sample

EQL = 11.5 µg sulfuryl fluoride / sample

NA = not analyzed

Sample #19 was not used.

F = front tube.

B = back tube.

µg = microgram

Sample ID (Sample identification) numbers followed by the letter C are collocated samples for the samples with the corresponding number.

Site location identification:

EI:	East Inner
EO:	East Outer
N:	North
NEI:	Northeast Inner
NEO:	Northeast Outer
NWO:	Northwest Outer
NWI:	Northwest Inner
SE:	Southeast
SI:	South Inner
SO:	South Outer
SWO:	Southwest Outer
SWI:	Southwest Inner
W:	West
XNE:	Extra Northeast
XNW:	Extra Northwest

Table 2: QC Sample Results
Sulfuryl Fluoride Application

Quality Control Type	Laboratory ID	Date Analyzed	Sulfuryl Fluoride (µg/sample)	Percent Recovery
Lab Spike (55.2 µg)	LS-1	7/14/04	51.7	94
	LS-2	7/14/04	51.8	94
	LS-3	7/14/04	57.7	105
	LS-4	7/14/04	58.8	107
Trip Spike (55.2 µg)	TS-SF-1	07/14/04	52.3	95
	TS-SF-2	07/14/04	49.4	90
	TS-SF-3	07/14/04	54.5	99
	TS-SF-4	07/14/04	52.7	96
ARB Spike (395 µg)	FS 6/30	07/14/04	331	84
	FS 7/1	07/14/04	324	82
Trip Blank	SF-FB	7/14/04	DET	

Notes:

ID Identification
µg Micrograms